# Water Use in Industries of the Future: Petroleum Industry<sup>1</sup>

# Contributed by:

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# 7.1 Petroleum Industry

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# 7.1.1 How Water is Used in the Petroleum Industry

### **Overview**

Water use in petroleum refining occurs in two main areas: steam production and cooling service. Some water is also used to remove water soluble inorganic compounds from hydrocarbon streams. Steam is sometimes used in direct contact with hydrocarbons, which results in production of process wastewater.

Cooling water makeup and boiler feedwater makeup each typically account for about 40-45 percent of the total water consumption, with utility water and potable water making up the balance. In terms of actual end use, process water demands are often satisfied with steam condensate, which translates into an increase in boiler feedwater makeup rate. Process wastewater originates primarily from steam or condensate used in direct contact with the process stream or as cleaning or flushing water. Most of the water consumed is lost through evaporation, with only about 20 percent discharged as wastewater. Process wastewater typically accounts for about two-thirds of the wastewater and cooling tower blowdown about one-third. These water and wastewater rates apply to refineries that use closed circuit cooling water systems and that are located in temperate regions of North America. Refineries that use once-through cooling or that are located in areas with extremes of temperature or humidity have different rates.

# **Typical Refinery Water Uses**

The flow of water through a typical refinery is shown in Figure 7.1-1.

#### Consumptive uses

Consumptive use of water means water that is drawn from the local source (river, lake, well, or municipal supply) and not returned. It is either put into the final products, or it is loss to the atmosphere through evaporation.

The total amount of water used in refineries in 1992 was estimated by one source to average 65 – 90 gallons of water per barrel of crude oil (Energetics, 1998). An extensive CH2M HILL study of a major refinery and petrochemical complex identified the distribution of water uses as shown in Figure 7.1-2.

Evaporative losses account for essentially all of the consumptive use in petroleum refining representing loss of both water and energy, as process cooling constitutes rejection of energy.

In a plant where energy efficiency is maximized, heat rejected from the process at one temperature is used in another process. When no further application of low temperature energy exists, the excess heat is rejected to the atmosphere. Some heat is rejected by direct transfer to the atmosphere through air fin cooling, while the rest is rejected through a cooling water system. Conditions that favor air fin cooling are high process temperature relative to atmospheric dry bulb temperature and limited availability of water for cooling. Process and environmental conditions specific to each site determine the amount of air cooling versus water cooling used, however cooling water represents a significant water use at all sites. In a typical open cycle cooling water system, the cooling towers produce the evaporative losses. As shown in Figure 7.1-2, makeup of water to the cooling towers can represent nearly half of the water demand in a refinery. A small additional evaporative loss occurs when steam leaks from equipment or piping or is vented to remove non-condensable gases.

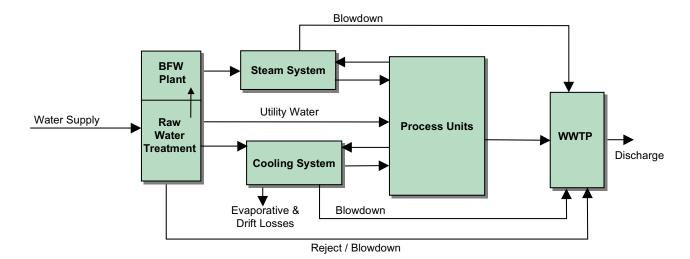


FIGURE 7.1-1 Flow diagram showing the flow of water through a typical North American refinery that uses a closed circuit cooling water system.

#### **Return Flow**

Return flow refers to water that is drawn from the local source, used in the production process or in utility functions such as heating or cooling, and then returned to the local source (river, watershed or aquifer). The net water drain on the local environment is zero; however, water quality might be affected.

#### **Contact Water**

This is water that comes into contact with the product, and has product or process residuals in it when it is returned to the environment. Contact water originates with crude desalter units and direct steam contact in steam distillation units. All wastewater from the refinery process units has contact or potential contact with the product, either as part of the process or incidentally from its use as flushing and cleaning utility water or as runoff from process areas and contact with leaked or spilled product.

#### **Crude Desalter**

Water is used to extract water soluble inorganic compounds from the crude oil to prevent catalyst poisoning later in the process. Salty wastewater is also contaminated with water soluble organic compounds.

#### **Quench Water**

Some hydrocarbon reactions require a sharp drop in temperature as part of the process, in order to achieve good selectivity for particular products of reaction. In such cases, a circulating stream of direct contact cooling water, termed "quench water," is used to achieve the required temperature drop. This water is in direct contact with the product, and a portion

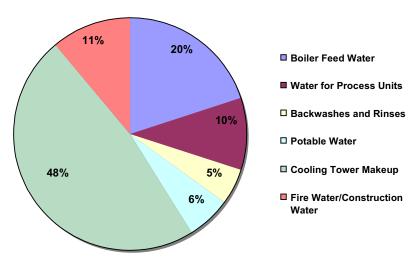


FIGURE 7.1-2 Distribution of major water uses at a large refinery and petrochemical complex (source: confidential CH2M HILL project).

of it is blown down to wastewater to maintain the quality of the circulating water.

# **Alkylation Wastewater**

In alkylation units, a solution of potassium hydroxide is used to extract the hydrofluoric acid catalyst from the hydrocarbon stream. The spent potassium hydroxide (KOH) stream is usually neutralized and discharged, although new processes to recover the fluoride and recycle the wastewater are being implemented.

#### Steam Distillation

Steam is used in multi-component distillation to improve the separation of the various hydrocarbons. Water is separated from the overhead stream immediately after the overhead condenser and is discharged as process wastewater.

### **Cooling Water Leaks**

Anytime the cooling water pressure is greater than the process pressure in a heat exchanger, internal leaks in the exchanger result in water entering the hydrocarbon stream and being discharged as process wastewater at the next separation point downstream. Leaks from the process into the cooling system will result in oily cooling water, which must be separated and would normally be diverted to the wastewater system.

#### **Non-Contact Water**

This is water that does not contact the product and does not contain product/process residuals, but it often is altered in other ways (residual heat in non-contact cooling water is common). This water could be used to aid the production process, or serve a utility function, such as plant heating or cooling.

Wastewater that has not contacted hydrocarbon product, but has nonetheless been altered significantly in composition includes boiler blowdown and cooling tower blowdown. Boiler blowdown is often used to supplement cooling tower makeup water or is discharged to the refinery wastewater treatment system. Cooling

tower blowdown normally contains only the inorganic constituents of the makeup water at increased concentrations and is commonly discharged without treatment, subject to confirmation of the absence of toxicity concerns from the cooling water treatment chemicals.

# **Once-through Cooling Water**

Refineries located close to large bodies of fresh water or to the ocean, particularly older facilities, often use water directly from the source for cooling and then discharge the heated water back to the same body of water. In theory, it is non-contact water; however; there is always a possibility of leaks from the process to the cooling water. In addition, the discharged water temperature can be a concern with respect to environmental conditions at the discharge point.

# **Potable and Sanitary Systems**

As for any large workplace, potable water is normally supplied to the offices, control rooms, maintenance areas, locker rooms, and anywhere else personnel are expected to spend any significant time. The water balance and wastewater characteristics are similar to potable water and sanitary wastewater anywhere and the volumes involved depend on the number of staff and the time they spend at the location.

Most refineries send sanitary wastewater to the local municipality to be treated separately from process wastewater, however in some refineries, sanitary wastewater is treated together with process wastewater in a biological treatment system. From a treatment perspective, this can work well, as the treatment process is similar and refinery effluents are often too dilute to sustain the biomass. The barrier to combined treatment consists mainly of the potential for the presence of pathogens in the sanitary waste. Adding a small flow of sanitary waste to a process wastewater treatment system may make it necessary to disinfect the entire stream before discharging it to a receiving body of water or to certain reuse applications.

# Quantities and Flow-through (Wastewater) Produced

A report prepared for the U.S. Department of Energy (Energetics, 1998) summarizes wastewater quantities and flow produced from various refining operations, using information from effluent limitations given by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419, originally promulgated in 1974. Table 7.1-1 summarizes wastewater generation by refinery unit.

# 7.1.2 Water Reuse Opportunities

# **Steam Systems**

Water is used in steam systems as a heat transfer fluid and is reused within the steam system as much as is economically feasible. Most steam is used in non-contact applications, such as indirect heat transfer and turbine drives, with the resulting condensate collected and returned for use as boiler feedwater. Water is lost through steam and condensate leakage, poor steam trap maintenance, and venting to remove non-condensible gases from the steam system. In some situations, such as steam used for tank heating in large tank farms that are dispersed over a wide area, condensate return is not economically feasible because of low flows and long distances. In these situations the condensate is lost. In some situations, an imbalance between steam requirements at various pressures and process heating loads or steam condensers can result in a need to vent steam, which is lost to the atmosphere. Where steam is used in direct contact, such as steam distillation, the condensate is not returned to the boilers. Water used for steam production must be low in dissolved contaminants, with the degree of purity depending on the boiler pressure. Since removal of dissolved material from boiler feedwater is never perfect, a small flow of water (blowdown) is discharged from the boilers to maintain the boiler water within design specifications for purity.

Because of the stringent quality requirements for boiler feedwater, steam systems are one of the least attractive options for reuse of wastewater, except for the internal reuse just described. Rather, contaminated or potentially contaminated steam condensate is a good source of water with low total dissolved solids (TDS) for applications such as crude desalting. Boiler blowdown, although it is contaminated relative to boiler feedwater, is a good source of water for reuse where low to moderate levels of TDS are not a problem. Use of blowdown from high-pressure boilers as feed for medium- and low-pressure boilers in a cascade mode is also a potential reuse option.

# **Cooling Systems**

A cooling water system typically has a high recirculation rate through the network of heat exchangers in the process units, back to the cooling towers, where the heat is removed by evaporative cooling, and then again to the heat sources. Heat is removed from the cooling water partly as sensible heat, but mainly through evaporation. The evaporative losses are by far the largest consumptive use of water in a petroleum refinery. Recent refinements to cooling tower design shift the heat balance toward a greater amount of sensible heat transfer and a smaller amount of latent heat transfer, which results in a smaller evaporative loss for the same cooling duty.

The composition of cooling water is subject to a considerable number of constraints to prevent corrosion, scale deposition, biological fouling, and solids deposition throughout the cooling system. In addition, cooling water is treated with one or more biocides and scale inhibitors for the same reasons. A portion of the cooling water (blowdown) is wasted, in order to limit the buildup of dissolved species caused by the removal of water through evaporation.

As a large net water user with relatively flexible quality specifications, cooling water makeup is a prime candidate for reusing water from other

**TABLE 7.1-1**Refinery Wastewater Flows

Process	Process WW Flow (gal/bbl of oil)	Comments
Crude distillation (atmospheric and vacuum)	26.0	Largest source: oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol
Fluid catalytic cracking	15.0	Largest source: sour wastewater from the fractionator/gas concentration units and steam strippers (high levels of oil suspended solids, phenols, cyanides, $H_2S$ , $NH_3$ )
Catalytic reforming	6.0	Process wastewater (high levels of oils, suspended solids, low hydrogen sulfide)
Alkylation	2.6	Wastewater from water-wash of reactor hydrocarbon products (suspended solids, dissolved solids, hydrogen sulfide) and spent sulfuric acid. Spent sulfuric acid – 13-30 lbs/bbl alkylate
Crude oil desalting	2.1	Largest source: hot salty process water (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids
Visbreaking	2.0	Largest source: sour wastewater from the fractionator (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids)
Catalytic hydrocracking	2.0	Largest source: sour wastewater from the fractionator and hydrogen separator (suspended solids, $H_2S$ )
Coking	1.0	Largest source: coke-laden water from decoking operations in delayed cokers (hydrogen sulfide, ammonia, suspended solids). Fluid coking produces little or no effluents.
Isomerization	1.0	Sour water (low hydrogen sulfide, ammonia), chloride salts, and caustic wash water
Ethers manufacture		Pretreatment wash water (nitrogen contaminants); cooling and alcohol wash water are recycled
Catalytic hydrotreating	1.0	Sour wastewater from the fractionator and hydrogen separator (suspended solids, $H_2S$ , $NH_3$ , phenols
Sweetening/Merox process		Little or no wastewater generated
Sulfur removal/Claus process		Process wastewater (hydrogen sulfide, ammonia)
Lubricating oil manufacture (de- asphalting, solvent extraction, de-waxing)		Steam stripping wastewater (oil and solvents), solvent recovery wastewater (oil and propane)

Source: Energetics, 1998. "Industrial Water Use and Its Energy Implications."

sources. Boiler blowdown, treated wastewater from either the refinery wastewater treatment plant or from a municipal treatment plant, and storm water runoff are all potential sources of cooling tower makeup.

# **Process Operations**

There are several opportunities for water reuse within the hydrocarbon processing units. Potentially oily condensate is suitable for use as desalting wash water. Stripped sour water from hydrotreating units typically has a high concentration of phenolic compounds, which are

returned to the crude, if the stripped sour water is used for desalter water makeup.

# 7.1.3 Water Use in Exploration and Production

# **Overview**

Water use in the exploration and production sector of the petroleum industry is negligible, with two exceptions, both in the field of enhanced oil recovery (EOR), which refers to processes used to remove more oil from the reservoir than what is possible by pumping only. Two specific EOR processes that are very water intensive are waterfloods and steamfloods.

#### Waterflood

A waterflood is an oil recovery technique that involves pumping water into an oil producing reservoir to replace oil that has been removed by primary production. The water serves, first, to fill the voidage and maintain the reservoir pressure, and second, once the water appears at the producing wells, to sweep unrecovered oil through the reservoir toward the producing wells.

At the surface, the produced water is separated from the oil and reinjected into the reservoir. A typical waterflood requires 100 percent makeup from other sources during the initial operation. As production proceeds, the amount of water produced increases and the demand for makeup water decreases. In some fields, the water-to-oil ratio can be as high as 10 or 20 to 1.

Water quality requirements for waterflood application are not stringent except on a few points. Suspended solids must be removed to quite low levels, depending on the permeability of the reservoir. Oxygen must be removed to prevent corrosion of the well tubing. The water must be rigorously disinfected to prevent the ingress of sulfur reducing bacteria.

Waterflood makeup water is a major opportunity for water reuse. Several floods use treated

municipal effluent for makeup water. Brackish non-potable groundwater and seawater are used in a number of applications, and high TDS wastewater would be a natural fit. A major barrier to reusing wastewater is the fact that many oil producing fields are not close enough to a suitable source of wastewater.

#### Steamflood

A steamflood is an oil recovery technique applicable to production of heavy crude (API 15 or lower) that is too viscous for reasonable recovery by simple pumping. Other heating methods are possible, but steam injection is by far the most common. High-pressure steam is injected into the oil bearing reservoir where it heats both the reservoir rock and the oil in it. The heated oil is much less viscous. Together with the condensed steam, it flows to production wells where it is brought to the surface with pumps, gas lift, or steam lift.

At the surface, the hot fluids (produced fluids) are separated, and the water fraction (produced water) is treated and reused to produce steam. Steam (for re-injection into the formation) at some facilities is raised from water of other origins, such as treated municipal effluent and brackish groundwater. Small development projects typically dispose of the produced water and use fresh water to raise steam. At most projects, steam is produced in a oncethrough oil field boiler at 80 percent quality (i.e., 80 percent vapor phase, 20 percent liquid) and injected as wet steam, or separated so that only the vapor phase is injected and the liquid phase is disposed of after recovery of the associated heat. Disposal of the liquid phase is typically by subsurface injection into a brackish aguifer or depleted oil reservoir. Depending on the nature of the reservoir rock and the technique used to contact the reservoir with steam, the produced water ranges in dissolved solids concentration from 2,000-3,000 mg/L to 8,000-10,000 mg/L, or even higher. Dissolved silica is typically present in concentrations of 200-300 mg/L as SiO<sub>2</sub>. Once through boilers

are used because they can tolerate high TDS concentrations and some dissolved silica, however water treatment is still a high cost component of the production facilities. Makeup water from another source is required to start up the process, to compensate for water retained in the reservoir and for wastewater that cannot be reused.

# 7.1.4 Relationship of Water to Energy

# Water Use and Associated Energy Costs

The major use of water in a refinery is for energy transport, either in the steam system or the cooling water system.

#### Steam Generation, Distribution and Use

Water is used to transfer heat from fuel or process heat sources to a wide variety of energy users. Losses occur at a number of points; wastewater from the water treatment system, leaks of water or steam throughout the system, deliberate discharge of contaminated condensate, steam vents, and at locations where recovery of steam condensate is simply not economic. In general, the amount of water lost will be in proportion to the thermal duty of the steam system. Factors other than system size that will influence the amount of water lost include:

- The quality of the water source and the treatment processes used will affect the amount lost as wastewater.
- The cost of energy will influence how much maintenance is done to prevent steam and condensate leaks and the investment made to recover small condensate flows.
- The age of the facility will influence the cost of maintenance and therefore the effectiveness of leakage control measures.

Since water and steam in a steam generation and distribution system is quite pure, steam leaks could be considered a return of clean water to the environment at the atmospheric vapor portion of the hydrologic cycle.

## **Cooling Water Systems**

The consumptive use of water in cooling systems is tied closely to energy efficiency with an inverse relationship. Virtually all consumptive use is evaporative loss, and all cooling loads represent lost energy. The latent heat of water evaporation is approximately 1,000 BTU/lb, so in round numbers, every gallon of water evaporated is equivalent to 8,300 BTU or 2.4 kWh of lost energy.

Evaporative loss is also at return to the hydrologic cycle at the atmospheric vapor point and does not carry contamination with it. Drift loss does carry contamination with it and and is difficult to control after it leaves the tower. Cooling towers are now being designed to minimize drift loss.

# 7.1.5 Water Reuse Practices and Challenges in the Industry

# Overview of Water Reuse Practices and Challenges

Water reuse planning in the petroleum industry is moving from water management plans that rely on consumption of raw water and discharge to the environment to plans that incorporate higher utilization efficiencies. Strategies for tightening up the water balance include:

- Internal treatment and reuse of wastewater
- Design of cooling towers to increase sensible heat transfer and thereby reduce evaporative losses
- Treatment of cooling water makeup or sidestream to minimize the amount of blowdown required
- Increased use of wastewater from external sources for water supply

The practice of using water evaporation as a final heat sink results in not only the largest net water consumption rate, but also the biggest challenge for the internal recycling of wastewater. As water evaporates, contaminants accumulate in the remaining water in the system and must be removed. Suspended material can be filtered out and calcium and magnesium salts can be removed by precipitation. However, sodium chloride and sulfate and other highly soluble salts can be removed only by very expensive and energy intensive means, such as evaporation. Membrane processes can concentrate these highly soluble salts, but not remove them. The use of evaporative cooling therefore results in the discharge of saline wastewater to the surface or to a suitable deepwell disposal formation, or in the accumulation of waste salt on the surface, no matter how thorough the treatment for other contaminants and the internal recycling of water.

### **Case Study**

A good example of how water management strategies in petroleum refining are changing can be found in a recent refinery expansion. In this case, a refinery originally built in the 1950s was being modified to accept a higher American Petroleum Institute (API) gravity feedstock, reduce the sulfur in gasoline and diesel fuel products, and expand overall capacity. The refinery is situated near a major river and a city with a population of approximately 1 million.

Figure 7.1-3 shows the major water flows for the existing refinery, before the expansion and before a new water management plan took effect.

In addition to the usual objectives of low cost, reliable, safe operation, etc., objectives for the revised water management plan included the following, in spite of a major increase in the steam rate and cooling load.

- Remain within the existing water withdrawal licensed volume
- Remain within the capacity of the existing subsurface injection well capacity
- Be confident of being able to obtain a wastewater discharge permit

The planned expansion includes the following water management items, intended to minimize the use of river water and to limit the amount of deepwell disposal.

Demineralization of all boiler feedwater, via a system based on reverse osmosis (RO), to meet 1,500 psi specification, improve the operation, and reduce the amount of blowdown from the 600 psi boilers

- Softening of the RO reject stream from boiler feedwater treatment for use as cooling tower makeup
- Use of deepwell disposal for high TDS wastewater only.

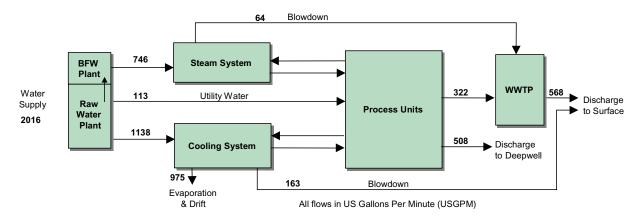


FIGURE 7.1-3
Flow diagram showing the flow of water through a typical North American refinery that uses a closed circuit cooling water system

- Major upgrade of refinery wastewater treatment system.
- Reuse of refinery effluent as cooling tower makeup water.

Figure 7.1-4 shows the major flows after the expansion and implementation of the revised water management plan.

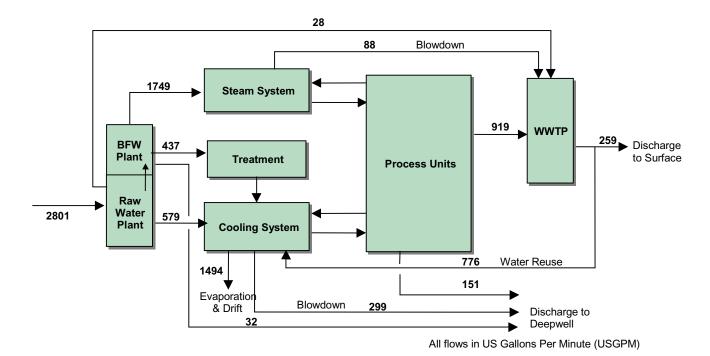


FIGURE 7.1-4
Major water flows for the expanded refinery, after implementation of a new water management plan.

# 9.1 References

Energetics, Inc. 1998. Energy and Environmental Profile of the U.S. Petroleum Refining Industry. Energetics, Inc., Columbia, Maryland. Prepared for U.S. Department of Energy, Office of Industrial Technologies, Washington, D.C. Energetics, Inc., Columbia, Maryland.